Geochemistry and mineralogy of rare earth processing

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The geochemistry and mineralogy of REE deposits is diverse, from carbonatite-related deposits, alkaline rocks, mineral sands and ion adsorption clays to potential by-products of phosphate and bauxite, and re-use of waste materials. Despite the large number of prospects that have been explored recently, very little additional REE production has started. A major challenge is to design effective, cost-efficient and environmentally-friendly processing and extraction. Processing flow sheets have to be constructed carefully for each deposit. Translating geochemistry and mineralogy studies, including quantitative mineralogy results, into processing characteristics can be illustrated using results from the Songwe Hill carbonatite, Malawi. Combining results with other published data then allows us to make some general conclusions about the common REE ore minerals and their geological environment, including the REE fluorcarbonate series, monazite and xenotime. The use of chemicals for REE extraction is often the largest environmental burden to mitigate. A new issue is that certain REE, such as Ce, are in oversupply, and are not being recovered in some proposed processing flowsheets. It will be important to understand the environmental and commercial implications of this development.

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Heterotrophic bioleaching of mine tailings

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From the early days of the Industrial Revolution, primary mining and metal processing industries in Europe have, and continue to landfill and/or stockpile significant quantities of metal containing tailings, which often represent an environmental and health risk. However, this 'tailings problem' may be seen as an opportunity and by valorising these historical and fresh tailings can provide a new source of sustainable critical raw materials. Traditional hydrometallurgical methods for the recovery of metals involve large quantities of concentrated acids or alkalis, and often require re-landfilling of the residual fractions. Therefore we propose an alternate strategy for the recovery of metals from mine tailing using heterotrophic bioleaching, via acidic biolixiviants.

To further our understanding of heterotrophic bioleaching, we first characterised organic acid production by several yeast and fungal cultures, Candida Viswanathi, Saccharomyces Cerevisiae and Aspergillus Niger and found that a mix of oxalic, gluconic and citric acids were produced. Subsequently, we investigated the impact of carbon, nitrogen, phosphorus, amino acid, vitamin and trace metal sources and concentrations on organic acid production. Furthermore, we attempted a bio-encapsulation method for novel application to promote bio-lixiviant formation. Finally, we tested the bioleaching potential of our cultures with several metallurgic mine tailing residues. These results will be discussed in the context of bioleaching of mine tailings as a foundation for future sustainable metal recovery.
The mass flow calculations as an indicator of the recovery potential of valuable elements from the sewage sludge incineration residues

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The amount of sewage sludge (SS) produced in wastewater treatment brings the challenges to its proper management. Since landfilling is no longer recommended due to the fact that it contains harmful elements and toxic organic substances and it is considered as hazardous material, SS incineration is regarded as safer and cost-effective option for its management. The main purpose of incineration is to reduce volume and possible negative influence of SS on the environment through disinfection and detoxification at temperatures of about 850-900°C. As a result of incineration fly ash (FA), air pollution control residues (APC) and flue gas with suspended dust (FG) are produced.

Out of 76,374 t of sludge (100%) incinerated in 2015 in one of the sewage sludge incineration plant located in the ca. 1 mln inhabitants city in Poland, 4,452 t of FA (6%), 836 t of APC (~1%) and 0.14 t of FG (0.0002%) were produced.

Based on mass flows calculations (mass per year) and results of chemical analysis, the recovery potential of Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se and Zn was determined.

Even though the measured concentrations of Cd, Cr, Cu, Ni and Zn indicated their accumulations in the FA and of Hg, Pb, Sb and Se in the APC (especially noted after removal of soluble mineral phases, which precipitated as a result of addition of NaHCO₃ in the APC purification process), the mass flow calculations indicated that 99% of Cd, Cr, Cu, Ni, Pb, Sb and Zn accumulated in the FA, what gave totally 25 t/y. Se was fractionated evenly between FA and APC (ca. 25 kg/y in each) whereas 99% of Hg (~1 kg/y) concentrated in the APC.

The measured content of elements is not a reliable indicator of their recovery potential. It is possible to assess it by determining the share of elements in the bulk volume of incinerated SS. Nevertheless none of this elements formed own mineral phases but it was rather dispersed within other minerals and amorphous substances, therefore their recovery require the development of specific recovery methods.

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**Time-related diversity of municipal bottom ash chemical composition**

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The chemical composition of municipal solid waste incineration bottom ash (BA) is related to a local waste stream composition. Thermal treatment causes accumulation of non-combustible fraction and final products of the process are characterised by certain level of diversity even within one instalation. The BA is a heterogenous material composed of amorphous and mineral phases together with metallic fragments and other residual components.

Production of large amounts of the BA and its characteristics brings attention on its possible application potential e.g. as valuable elements resource or as raw material in concrete and ceramic industry.

The aim of this study was to investigate time-related changes over a four years period in chemical composition (determined using ICP-MS and OCP-OES methods) of BA collected from municipal waste incineration plant in Poland.

The BA is a material rich in Si (22-28 wt%), Ca (9.5-12.5 wt%), Fe (1.5-6.8 wt%), Al (3-5 wt%) and Na (3-5.2 wt%). Changes observed in minor metallic elements concentrations were relatively more significant than within the major elements. The variation range between lowest and highest content of metallic elements often exceed their average content in the BA (Figure 1).

![Content of metallic elements in the BA.](image)

BA is characterised by high variability of chemical composition over time what makes it monitoring important in the process of BA valorisation prior to it further usage.

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Chemical and biogenic organic acid leaching of low-grade, polymetallic primary ores and secondary industrial residues

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Europe does not possess vast, easily accessible deposits containing critical and economically valuable metals. However, it does have substantial amounts of low-grade, polymetallic primary ores and secondary industrial residues (tailings, sludges, slags and dusts), which contain significant concentrations of various metals.

A broad screening of metal recovery from these materials is presented for metal recovery of Zn, Cu, Cr and Ni. First using synthetic organic chelating organic acids (citric acid, gluconic and oxalic acid) as chemical analogues to those produced via microbial heterotrophic respiration. Followed by application of biogenic organic acids produced by relatively benign yeast cultures of Candida Viswanathii and Saccharomyces Cerevisiae.

An extensive fractional factorial design of experiments (DOE) for fast track screening, evaluation and optimization of bioleaching phenomena is presented. Testing pulp density, mixing speed (50 – 150 rpm), various mixtures of citric, gluconate and oxalate acids, leaching time (3 – 20 hrs) and organic acid concentrations (50 – 150 mM). Based on best case bioleaching, further process and rudimental modelling of bioleaching kinetics and mass transfer are also discussed.

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COLUMN EXPERIMENTS AND NUMERICAL MODELLING FOR IN-SITU LEACHING OF SANDSTONE-HOSTED COPPER DEPOSIT

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The BioMOre EU Horizon 2020 project (www.biomore.info) aims at developing “deep-in situ biomining” technology which have recently received an increasing attention from research and industry as a cost effective method for recovering metals from deep buried deposits. It consists in injecting a leach solution into the targeted ore body for dissolving base metal bearing minerals, collecting the pregnant solution and in regenerating the leach solution thanks to micro-organisms. This technology is being experimented at reactor scale on a Kupferschiefer copper deposit in Poland as part of the BioMOre project.

In this contribution, we present laboratory column experiments investigating the effect of a leaching solution in contact with copper bearing ore crushed at different grain sizes in suitable micro-organism environment conditions. Three stages including (i) water washing, (ii) acid leaching, and (iii) ferric-acid leaching, are successively implemented for progressively dissolving salts, carbonate minerals, and finally copper bearing sulfides.

Models have been implemented in PhreeqC in parallel to the column experiments. They consider a one-dimensional double porosity transport model, where dissolution reactions are described by kinetics. We rely on BRGM’s Thermodem databases [1]. Key parameters such as proportion of advective and diffusive phases, and effective diffusion coefficients were refined by fitting experimental results.

The leaching process was then simulated in 3D at a deposit mesh scale by coupling one-dimensional PhreeqC models with a streamline-based fluid flow simulation approach. Such models will be further used within the BioMOre project for optimizing well-design planning and recovery forecasts.

Promoting early REE separation during ore leaching: an investigation through controlled synthetic crystal dissolution experiments

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In many REE deposits, the carrier minerals display extensive solid solutions that induce variation in surface and crystal properties which can significantly impact flotation and leaching behaviors. In this context, controlled experiments on synthetic crystalline systems, where structural and chemical variables can be isolated, provide opportunities to better understand important interfacial mechanisms that control collector surface interaction and mineral dissolution. Our study focuses on the compositional space of REE-orthophosphates through the synthesis of analogues along well-defined substitutions with the objective of improving flotation selectivity and identifying optimal dissolution paths.

Here we report the progress of experiments designed to investigate factors that promote early separation of the different REEs during initial orthophosphate cracking in alkali hydroxide solutions. Single natural and synthetic crystals of monazite and xenotime are exposed to caustic solutions of various compositions at pressures up to 20 MPa and temperatures ranging from 140 to 300°C. The impact of sequential dissolution cycles where crystals are periodically quenched and immersed in a fresh solution are also examined. The nature of the resulting REE hydroxide leached layer is characterized by micro X-ray diffraction, field-emission electron probe X-ray microanalysis, dynamic secondary ion mass spectrometry, and transmission electron microscopy.

Our current results indicate that, through a fractional dissolution process, there exist pressure-temperature paths where efficient REE selectivity is achieved with the larger trivalent lanthanides reporting to the solid hydroxide leached phase while partitioning of the heavier REEs in solution increase progressively with decreasing trivalent ionic radii. Optimization of this dynamic dissolution approach could minimize the downstream hydrometallurgical challenges typically associated with REE separation. However, this requires an understanding of the nature and relative thermal stability of specific dissolved REE species. Consequently, strategies for in-situ real-time spectroscopic measurements in high-temperature caustic environments are being developed and preliminary results will be discussed.
Mineralogical constraints in ore processing of Li-rich pegmatites

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In recent years, lithium (Li) demand is increasing. The main ores for Li are brines and also crystalline rocks rich on Li silicate minerals and/or phosphates. In Europe, there are some regions with good potential for Li ore production; the most important deposits are granite pegmatites and greisens and the most important minerals are spodumene, petalite, lepidolite and zinwaldite.

Under the scope of project FAME (Flexible and Mobile Economic Processing Technologies), that focuses on improving processing technologies and to recover valuable materials from low grade and/or complex feedstock’s ore, two European Li ores are being investigated: lepidolite from Gonçalo (1.2% Li₂O) (Portugal) and spodumene from Keliber (1% Li₂O) (Finland).

Froth flotation is the most suitable process to produce spodumene and lepidolite concentrates and it was tested in the two referred ores, after milling below 150µm for liberation purposes. During the processing of the two ores, it was not possible to maintain a Li₂O grade, close to the mineral stoichiometry, in the concentrates, even for low recoveries: for lepidolite, 3.9% Li₂O is the maximum grade obtained for 37% Li₂O recovery, remaining practically constant, even for high recoveries; spodumene flotation exhibits a maximum grade at 5.2% Li₂O under 35% recovery, which drops significantly to 2% Li₂O for 60% recovery.

At this point, it was necessary to find out a reasonable justification for these observations, from a mineralogical point of view. Studies on Gonçalo aplitic-pegmatites reveal that fine lepidolite (0.5 to 2 mm) exhibits albite and quartz micro-inclusions (<100 µm). At Keliber, spodumene occurs in the form of poikilitic crystals with graphic and symplectic intergrowths with quartz which tends to be coarser (up to 250 µm long) and sub-angular in the centers of large spodumene crystals. However, these often grade into a symplectic intergrowth of minute and rounded vermicles, myrmekite-like, in spodumene at the contact with feldspar grains. These myrmekitic textures commonly grade into fibrous intergrowths of spodumene + quartz at the margins. The described mineral associations can be one of the reasons justifying low degrees of liberation of ore minerals.